

From complex fluorides to CFC alternatives — an account of fluorine chemistry at Glasgow

John M. Winfield*

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK

Abstract

Advances in the areas of complex fluorides, high-oxidation state fluorides, perfluorocarbon ligand complexes, solvated cations and radiotracer catalytic studies made in the city of Glasgow are described. © 1999 Elsevier Science S.A. All rights reserved.

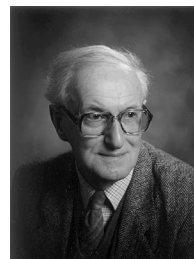
Keywords: Fluorine; Catalytic; Glasgow; Spectroscopy

1. Introduction

The author's first significant encounter with an inorganic fluoride occurred in 1958, not in a laboratory or lecture theatre, but during an inorganic chemistry tutorial given to four or five young 1st-year undergraduate students by David Sharp, who at that time was a junior member of staff at Imperial College, London. The chemical in question was BrF_3 , home-made and contained in a mild steel pot. David Sharp occupied a small lab-office (the organisation of which left something to be desired!) in the Chemistry Department at I.C., and the BrF_3 container was inadvertently disturbed by one of us during a tutorial; luckily it did not fall over, otherwise this account would probably not have been written! Shortly afterwards, in 1961, I was one of the several postgraduate students who moved with David from London to Glasgow, to what was then the Royal College of Science and Technology — a well-respected institution which became Strathclyde University¹ in 1964. The following account describes some of the fluorine chemistry carried out in the City of Glasgow that, at least in my opinion, can reasonably be described as 'landmarks'. Where appropriate, I have placed this work in context by reference to earlier studies carried out either at Cambridge University, where David Sharp was a student, or at Imperial College.

All UK fluorine chemists of the author's vintage have been influenced profoundly by the famous fluorine school founded by H.J. Emeléus² at Cambridge University in the

immediate post-World War II period^{3,4}. In particular the work of A.G. (Alan) Sharpe, David Sharp's Ph.D. supervisor at Cambridge, exemplifies the importance of synthesis coupled with physico-chemical studies.



A.G. Sharpe

This has been a recurring principle in much of the Glasgow work, which has regularly involved 'physical' and 'organic' chemistry as well as 'inorganic'. A thematic approach has been adopted in this account, and while the work is described in an approximate chronological order, the overlaps, both in time and location, are considerable.

2. Complex fluorides

The first general synthetic route to ternary fluoride complexes was developed by the Cambridge School and reported

³Note that Emeléus' influence spread globally. The tradition of enhancing the activities of the inorganic school through overseas research fellows and other visiting researchers that he established in the very early days at Cambridge, continued for many years. Those who contributed to fluorine chemistry included Ang How Ghee (Singapore), R.G. Cavell (Canada), H.C. Clark (Canada), A.F. Clifford (USA), W.I. Cullen (New Zealand), J. Grobe (Germany), A. Haas (Germany), A.G. MacDiarmid (USA), T.A. O'Donnell (Australia), R.C. Paul (India), J.M. Shreeve (USA), L.E. Smythe (Australia), E.G. Wazaschewski (Poland) and S.M. Williamson (USA).

⁴See Appendix A for A.A. (Alf) Woolf's memoir on those early days.

*Tel.: +44-141-330-5134; fax: +44-141-330-4888.

E-mail address: j.winfield@chem.gla.ac.uk (J.M. Winfield)

¹Strathclyde was one of the ancient Scottish Kingdoms and was used to name the region of local government covering the Western part of Scotland.

²Harry Julius Emeléus, CBE, FRS (1903–1993).

by Emeléus, Sharpe and Woolf in a series of papers published in the late 1940s and early 1950s [1–7]. Solvolysis of halides or oxides in liquid BrF_3 was rationalised [2] on the basis of the postulated self-ionization $2\text{BrF}_3 \rightleftharpoons [\text{BrF}_2]^+ + [\text{BrF}_4]^-$ with acid-base reactions, for example, between $\text{A}[\text{BrF}_4]$, $\text{A} = \text{K}$ or Ag , and $[\text{BrF}_2][\text{SbF}_6]$ or $[\text{BrF}_2]_2[\text{MF}_6]$, $\text{M} = \text{Sn}$ [2] or Ti [4], leading to complex fluoride or oxo-fluoride products. A large number of ternary fluorides, particularly those containing d-block metals have been prepared in this way. In some cases, decomposition of $[\text{BrF}_2]_2[\text{MF}_6]$ adducts yields the parent tetrafluoride, e.g., PtF_4 [4], but preparation of binary fluorides by this route may result in impure products that contain bromine. The oxidizing power (sometimes uncontrollable) of liquid BrF_3 is illustrated by its reaction with a silver–gold metallic mixture to give $\text{Ag}[\text{AuF}_4]$ [3], an example that the author has sometimes found useful as an ‘unseen’ problem question in undergraduate examinations.

Despite its disadvantages, the BrF_3 route to ternary fluorides, A_2BF_6 or ABF_6 , remained popular for a considerable period. Reagents that were used as later alternatives include SF_4 [8], particularly useful for mixtures of Group 1 fluorides with metal oxides, sulfides or carbonyls. A third general route involves the reduction of d-block hexafluorides with iodide anion in liquid SO_2 , a route exploited by R.D. Peacock and co-workers which has been widely applied.

Although a brief collaboration between A.G. Sharpe and R.S. (Ron) Nyholm resulted in an early magnetochemical study of binary and ternary d-block fluorides [9], the main physical investigation of these compounds involved the determination of lattice parameters in the series A_2BF_6 and ABF_6 by X-ray powder diffraction. Early mapping of the A_2BF_6 , $\text{A} = \text{Group 1 cation}$, $\text{B}^{\text{IV}} = \text{Si, Ge, Ti, Mn, Ni, Pd and Pt}$, [10,11] by Cox and Sharpe was followed by an investigation of ABF_6 structural types [12] and culminated

in an exhaustive study of $\text{A}^{\text{IV}}\text{B}^{\text{IV}}\text{F}_6$ compounds, work carried out by R.D.W. Kemmitt, D.R. Russell and D.W.A. Sharp at Imperial College and Strathclyde [13]. Further, XRD powder work [14] on some $\text{Na}_2\text{B}^{\text{IV}}\text{F}_6$ compounds, extending the earlier study [11], followed shortly afterwards. As a result of these papers, appearing over the period 1953–1965, the crystal chemistry of ternary fluorides, particularly those containing d-block elements, was placed on a secure basis. The work, most of which is still regarded as correct, has informed subsequent studies of the spectra of these compounds and a selection of the results for $\text{A}^{\text{IV}}\text{B}^{\text{IV}}\text{F}_6$ complexes is presented in Table 1. It is ironic that this type of very detailed physico-chemical examination which had no obvious immediate ‘use’ would probably be very difficult to carry out in 1998 because of present UK funding policy.

Reliable recording CW IR spectrometers became available commercially during the mid-1950s and this spectroscopic method attracted David Sharp’s attention. He applied the technique to various weakly-basic, fluorine-containing anions such as $[\text{SO}_3\text{F}]^-$, $[\text{BF}_4]^-$ and hexafluorometallates (V), an interesting example being $[\text{Ph}_3\text{C}]^+$ salts of these anions in which a planar, propeller-like D_3 configuration was established for the cation [15]. A paper co-authored by R.D. (Ray) Peacock and Sharp from Imperial College proved to be a classic, judged by the number of citations it received subsequently, and was one of the early attempts to apply simple symmetry considerations to the IR spectra of a variety of O_h and T_d fluorometallate anions in the solid state [16]. Subsequent work, at Strathclyde, treated IR spectra (now routinely available down to 250 cm^{-1}) in terms of site symmetry [17] and factor group [18] analyses and culminated in a detailed spectral examination by Andrew Lane of cubic and orthorhombic perovskite fluorides, ABF_3 , including a study of the low temperature cubic \rightarrow orthorhombic (or tetragonal) phase change in KMnF_3 [19].

Table 1
Structures adopted by $\text{A}^{\text{IV}}\text{B}^{\text{IV}}\text{F}_6$ complex fluorides^{a,b}, reproduced with permission from Ref. [13]

B^{V}	A^{I}						
	Li	Na	Ag	K	Tl	Rb	Cs
P	R_1	C_1	C_2	C_2, R_2	C_2	C_2	C_2
As	R_1	R_1	C_2	R_2	R_2	R_2	R_2
V	R_1	R_1	T	R_2	R_2	R_2	R_2
Ru	R_1	R_1	T	R_2	R_2	R_2	R_2
Ir	R_1	R_1	T	R_2		R_2	R_2
Os	R_1	R_1	T	R_2		R_2	R_2
Re	R_1	C_1		T		R_2	R_2
Mo	R_1	C_1		T	R_2	R_2	R_2
W	R_1	C_1		T		R_2	R_2
Sb	R_1	C_1	T	T	R_2	R_2	R_2
Nb	R_1	C_1	T	T	R_2	R_2	R_2
Ta	R_1	C_1	T	T	R_2	R_2	R_2

^a C_1 : cubic NaSbF_6 structure; C_2 : cubic CsPF_6 structure; R_1 : rhombohedral LiSbF_6 structure; R_2 : rhombohedral KOsF_6 structure; T: tetragonal KNbF_6 structure.

^b Ordering of A^{I} ($l \rightarrow r$) and B^{V} ($t \rightarrow b$) according to increasing size.

This section would be incomplete without an acknowledgement of the contribution made by A.G. Sharpe to the development of a thermodynamic basis to inorganic fluorine chemistry, being applied not only to complex fluorides [20] but also to the energetics of halogen-exchange reactions involving ionic binary fluorides [21] and to the solvation of the F^- anion [22].

3. Substituted derivatives of high oxidation state fluorides

The move from England to Scotland in 1961 coincided with an expansion of Sharp's research interests, to include molecular chemistry of non-metal fluorides, and the period 1961–1979 was characterised by a steady research output, initially from the Royal College (Strathclyde) and later from both of the chemistry departments at Glasgow and Strathclyde. However, the first person in Scotland to carry out research in this area was probably D.S. Payne at Glasgow University. Douglas, a graduate of Imperial College and Cambridge where he was a student of Emeléus, was primarily a phosphorus chemist, but his interests included mixed halide derivatives [23], for example the preparation of salts such as $[PCl_4][PCl_5F]$ [24].

To some extent this new research was prompted by the increasing availability of fluorides such as SF_4 and PF_5 , the former available as gifts from ICI or DuPont, the latter generated from Phosforogen A (Ozark Mahoning), an aryldiazonium $[PF_6]^-$ salt. A 60 A fluorine cell loaned by ICI was in regular use and the DuPont synthesis of SF_4 , from $SCl_2 + NaF$ in acetonitrile, often employed. The advent of ^{19}F NMR spectroscopy was crucial to this work, the department taking delivery of its first spectrometer, 40 MHz with a permanent magnet, in ca. 1963. I spent many happy (!) hours, usually in the evenings when instrument performance was more reliable, recording ^{19}F spectra of both perfluorocarbon derivatives and transition metal fluorides. My other abiding memory of the early-sixties is being asked to construct a vacuum line suitable for the manipulation of volatile fluorides without the services of a professional glass-blower. As with many self-taught glass-blowers, the results were not always pretty but I was very lucky that David Russell (a 2nd year Ph.D. student) was accomplished and he often helped me out. Our studies of substituted derivatives ranged over both p- and d-block fluorides and were carried out during the period 1961–1979. A selection of the molecules prepared is contained in Fig. 1.

Phosphorus–fluorine chemistry received a significant boost with the arrival of George Fraser as a postgraduate student. He argued that there were analogies to be drawn between boron halides and PF_5 , and proceeded to demonstrate this by synthesizing secondary amine- PF_5 adducts which could be decomposed thermally to give dialkylamino fluorophosphoranes such as $PF_4(NMe_2)$ and $PF_3(NMe_2)_2$ [25]. Complex formation between PF_5 and various Lewis bases proved to be a very productive area for study; several

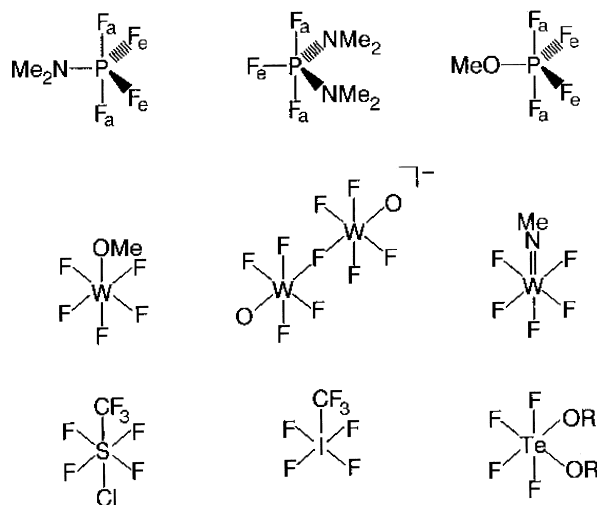
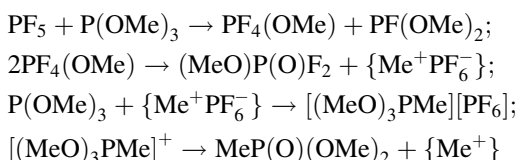


Fig. 1. Some of the substituted derivatives prepared at Glasgow in the 1960s and 1970s (identified by NMR spectroscopy).

P–F bonded adducts were characterised, $P(NMe_2)_3$ being an alternative reagent for the introduction of the $-NMe_2$ ligand to P^V [26]. Aminolysis of PF_5 or PF_3 using primary amines was studied subsequently with similar results [27]. A highlight from this period is work on the $(MeO)_3P.F_5$ adduct, which proved too unstable thermally to be characterised, but whose decomposition led to a rich chemistry, the main elements of which can be rationalised by the equations [28]:



The last reaction proceeds by a second-order autocatalytic process and corresponds to the decay of the intermediate of the Michaelis–Arbuzov rearrangement of $P(OMe)_3$. An additional product, $(MeO)(Me)P(O)F$, is believed to be formed by a similar rearrangement of $PF(OMe)_2$. An analogous investigation based on $P(OEt)_3$ was terminated abruptly after George Fraser and a fellow student, Donald Barclay, were forced to pay an unexpected visit to Glasgow's Royal Infirmary with symptoms attributable to nerve gas exposure.

Other P–F substituted derivatives prepared included $PF_4(SMe)$, using Me_3SiSMe [29], $F_2P(S)OP(S)F_2$ [30], $PF_4N(Me)PF_2$ [31] and $F_2(O)PN(R)P(O)F_2$ [32]. Sharp's group made a substantial contribution, therefore, to the explosion in phosphorus–fluorine chemistry that occurred in the 1960s and early 1970s, and numerous links with other fluorine groups world-wide were established.

In 1965, when I was appointed as a junior lecturer at the University of Glasgow, molecular chemistry involving d-block high-oxidation-state fluorides was relatively undeveloped, and the possibilities in this area of chemistry, using aprotic organic solvents as reaction media were immediately explored. A reaction carried out between dimethyl

sulfite and WF_6 , designed to prepare the unknown $(\text{MeO})_2\text{SF}_2$ by utilising the capacity of WF_6 to form WOF_4 , led instead to the isolation of WF_5OME and very soon afterwards to most of the members of the series of methoxo-tungsten (VI) fluorides, $\text{WF}_{6-n}(\text{OME})_n$ [33], using Me_3Si -reagents, a route that was then in vogue for the preparation of substituted derivatives of many binary fluorides. ^{19}F NMR spectroscopy, including ^{183}W measurements made by using double resonance techniques developed by W. McFarlane and his coworkers, were crucial in making unambiguous structural assignments [34]. The other notable study in this area involved the tungsten (VI) chlorofluorides, $\text{WF}_{6-n}\text{Cl}_n$, work that was initiated by Mary Mercer⁵ and Ray Peacock at Birmingham University and carried out by George Fraser and his wife Joy (née Gibbs) after Peacock had been appointed to the Chair of Inorganic Chemistry at Leicester. The two series of compounds make an interesting contrast, the chlorofluorides readily undergoing redistribution reactions in solution below ambient temperature, while the methoxofluorides, which do not show this propensity, exhibit marked preferences for the *cis* configuration in $\text{WF}_4(\text{OME})_2$ and $\text{WF}_2(\text{OME})_4$. The differences were rationalised on the basis of the good π -donor properties of the MeO-ligand towards W^{VI} , an important factor also for the effect of the oxo-ligand in the NMR spectra of $[\text{WOF}_5]^-$ and the F-bridged dimer $[\text{W}_2\text{O}_2\text{F}_9]^-$ [34].

David Sharp moved from Strathclyde to Glasgow University in 1968 to occupy the newly-established Ramsay Chair and we began to collaborate in exploring further the chemistry of d-block fluoride substituted derivatives, notably diethylamido derivatives of WF_6 [35,36] NbF_5 , TaF_5 [37] and VOF_3 [38], pentafluorophenoxy derivatives of WF_6 [36] and alkylamidotungsten(VI) fluorides with their associated anions. This last group of compounds yielded superb ^{19}F NMR spectra, since the effects of ^{14}N coupling in the linear $\text{Me-N}\equiv\text{W}$ moiety were readily observed [39,40].

This activity in the d block did not mean that p-block fluorides were neglected. Although an early attempt to prepare methoxosulfur(IV) fluorides using $(\text{MeO})_2\text{SO}$ was unsuccessful due to their thermal instability, this was not a problem for phenoxy-analogues, hence the series $\text{SF}_{4-n}(\text{OPh})_n$ [41], $(\text{ArO})_n\text{S}(\text{O})\text{F}_{4-n}$, $n = 1-3$, $\text{Ar} = \text{aryl}$ [42] and analogous compounds based on CF_3SF_3 [43] were all characterised. Exploitation of the oxidative chlorofluorination of S^{IV} by CsF/Cl_2 led to the isolation of *trans*- $\text{CF}_3\text{SF}_4\text{Cl}$, free-radical addition of which to several alkenes and alkynes was demonstrated [44]. The heavier p-block elements, iodine and tellurium, respectively, were investigated at Glasgow (by me) and at Strathclyde (by Fraser, who was a lecturer there for a short time after Sharp's departure).

The work on iodine (V) derivatives was initiated by an attempt to extend the scope of a reaction reported by DuPont chemists who had demonstrated that $n\text{-C}_4\text{F}_9\text{I}$ could be

oxidised to $n\text{-C}_4\text{F}_9\text{IF}_4$ using ClF_3 below room temperature. Oxidation of CF_3I to CF_3IF_4 proved more problematic and was punctuated by numerous small explosions before we found the correct conditions [45]. Luckily Gerry Oates, the research student involved, was a very phlegmatic character! Decomposition of CF_3IF_4 appears to be catalysed by traces of I_2 and IF_5 , although the compound is more stable in this respect than the I^{III} analogue, CF_3IF_2 . However, substitution of F in CF_3IF_4 by OMe can be achieved, and the series $\text{CF}_3\text{IF}_{4-n}(\text{OME})_n$ was identified by ^{19}F NMR spectroscopy [45]. Other compounds of the R_FIF_4 type are more stable thermally, particularly where $\text{R}_F = \text{C}_6\text{F}_5$ [46], and evidence was obtained also for all members of the series $\text{IF}_{5-n}(\text{OME})_n$ except where $n = 2$ [47]. A characteristic of all the methoxo-iodine (V) fluorides studied is the liability of the fluorine, which is in marked contrast to the W^{VI} analogues.

George Fraser's interest in TeF_6 originated from his period with Ray Peacock at Leicester University, during which time they published several papers dealing with chloro-, dialkylamido- and methoxo-tellurium (VI) fluorides, and he continued work on the last class of compound during his second period at Strathclyde. The general synthetic route to $\text{TeF}_{6-n}(\text{OR})_n$, R is equal to various alkyl groups, involves reactions between TeF_6 and the parent alcohol, ROH [48–50], although the extent to which substitution of F occurs depends on the electronic properties of the R group [49]. *Cis* configurations for $\text{TeF}_4(\text{OR})_2$ are preferred over *trans*, though π -donor effects are less likely to be important here than with W^{VI} , and TeF_5OR compounds are powerful alkylating agents, better than $(\text{MeO})_2\text{SO}_2$ [51], a property shared by WF_5OME [33]. Hydrolysis of TeF_6 , if carefully controlled, leads to $\text{TeF}_{6-n}(\text{OH})_n$, $n = 1-4$ [52,53]; Si–O rather than O–H bond cleavage is observed also in reactions with Me_3SiOH or Ph_3SiOH .

The work during this very productive period was enriched enormously by discussions with visitors from other fluorine labs throughout the world. We enjoyed the friendly rivalry with Ray Peacock and his group at Leicester and the frequent visits from Reinhard Schmutzler (DuPont, thence Loughborough and on to Braunschweig), who not only gave us the experience of his 'rapid-fire' lecture delivery but also shared his NMR results.

4. Perfluorocarbon ligand complexes of d-block metals

Organometallic chemistry carried out during the 1970s by David Sharp and his students, notably Jack Davidson (presently a member of the Chemistry Department at Heriot-Watt University, Edinburgh), was centered on the behaviour of CF_3SSCF_3 and $\text{CF}_3\text{C}\equiv\text{CCF}_3$ towards a range of metal carbonyl and organometallic compounds. Photolytic generation of the $\text{CF}_3\text{S}^\bullet$ radical was exploited as a general route to metal-SCF₃ derivatives, for example $\text{CpMo}(\text{CO})_3(\text{SCF}_3)$, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $[\text{M}(\text{CO})_4(\text{SCF}_3)]_2$, $\text{M} = \text{Mo}, \text{W}$, and various

⁵See Appendix B for a memoir by Mary Mercer concerning events in Birmingham.

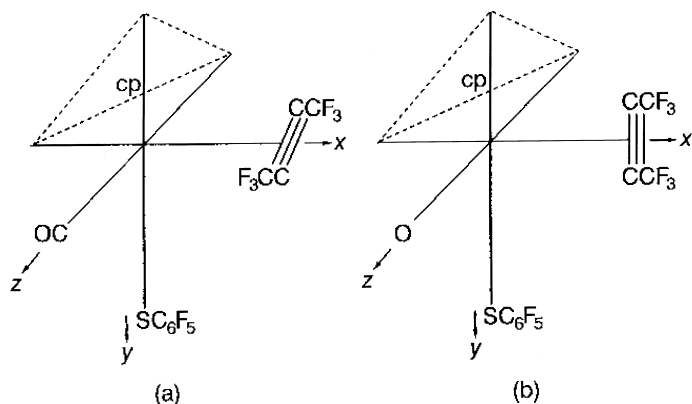


Fig. 2. Structures of (a) $[\text{CpMo}(\text{CO})(\text{CF}_3\text{C}_2\text{CF}_3)(\text{SC}_6\text{F}_5)]$ and (b) $[\text{CpMo}(\text{O})(\text{CF}_3\text{C}_2\text{CF}_3)(\text{SC}_6\text{F}_5)]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$). (Reproduced with permission, from Ref. [60]).

complexes originating from $\text{CpCo}(\text{CO})_2$. Analogous reactions were carried out also with $\text{C}_6\text{F}_5\text{SSC}_6\text{F}_5$, yielding products such as $[\text{CpCo}(\text{SC}_6\text{F}_5)]_2$ and $\text{CpCo}(\text{CO})(\text{SC}_6\text{F}_5)_2$ [54–56]. In parallel with this work, the photochemical addition of CF_3SSCF_3 to a range of olefins and fluoroolefins was explored, the products ranging from 1 : 1 adducts to medium-range telomers [57].

Sharp's interest in $\text{CF}_3\text{C} \equiv \text{CCF}_3$ as a potential ligand in organometallic chemistry originated at Imperial College [58]. Reactions between $\text{CF}_3\text{C} \equiv \text{CCF}_3$ or related alkynes and the thiolate complexes mentioned above, lead to a variety of products, which include metathiolacyclobutenes and metallated vinyls; the $16e^-$ complexes, $\text{CpMo}(\text{R}_F\text{CCR}_F)_2\text{X}$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$, result from reactions of $\text{CpMo}(\text{CO})_3\text{X}$ [59]. The compounds $[\text{CpM}(\text{E})(\text{RCCR})(\text{SR}_F)]$, $\text{M} = \text{Mo}, \text{W}$; $\text{E} = \text{O}$ or CO ; $\text{R} = \text{CF}_3, \text{Me}, \text{Ph}$; $\text{R}_F = \text{CF}_3, \text{C}_6\text{F}_5$, which result from reactions of $\text{CpM}(\text{CO})_3(\text{SR}_F)$ with alkynes exist in two different geometries (Fig. 2) which was demonstrated using low temperature NMR spectroscopy

[60] and confirmed subsequently by X-ray crystallography. The versatility of $\text{CF}_3\text{C} \equiv \text{CCF}_3$ and its analogues is evident from these examples, and progress would not have been possible without structural determinations by X-ray crystallography for definitive identifications. A tetrameric Ni complex, $[\text{NiCp}(\text{CF}_3\text{C}_2\text{CF}_3)]_4$ [61] that was characterised in this way is shown in Fig. 3.

5. Binary fluorides in organic media-complexes, redox reactions and solvated cations

A distinctive feature of fluorine chemistry at Glasgow has been the use of dipolar aprotic organic solvents for solution studies on binary fluorides rather than the more obvious solvents anhydrous hydrogen fluoride, halogen fluorides or sulfur dioxide. The importance of cation solvation in determining the solubility of fluoroacid salts in organic solvents was recognised very early by Sharp and Sharpe, solvation of Ag^+ and Cu^+ by aromatic hydrocarbons being pertinent examples [62]. The approach was extended later to prepare solutions of Ag^+ or $\text{Cu}^{II}[\text{BF}_4]^-$ or $[\text{CF}_3\text{CO}_2]^-$ salts in Et_2O or MeNO_2 [63]. A very early report (in 1948) of a red solution formed by WF_6 in C_6H_6 attracted the author's attention during his Ph.D. work (I found out much later that Mary Mercer had been similarly intrigued during her doctoral work at Birmingham!) and this led to a systematic study of interactions between high-oxidation-state binary fluorides and π - or n -donor organic molecules that was carried out over several years. A range of interactions is possible, from very weak, of the contact charge-transfer type, which is observed for WF_6 and MoF_6 with both π - and σ -donors [64,65], to the conventional case of isolable Lewis acid-base complex formation between the pentafluorides of Mo [66,67] Nb , Ta [67,68] or U [69] and σ -donors such as pyridine (py), Me_2O or MeCN . The behaviour of IF_5 in MeCN is intermediate between these two extremes, since although an adduct is not isolated, there is Raman spectroscopic evidence for the perturbation of the IF_5 liquid structure by MeCN [70,71].

Our original objective in examining redox behaviour of high-oxidation fluorides such as WF_6 and MoF_6 in organic solvents was to develop the solution chemistry of fluoro-metallate anions without recourse to the specialised equipment that would be required for spectroscopic studies in anhydrous HF. Preliminary experiments established that both nitromethane and acetonitrile were suitable solvents to replicate the I^- anion reduction of WF_6 or MoF_6 , reactions which were known to occur in liquid SO_2 . Using R_4N^+ counter-cations produced very soluble salts, but side-reactions involving attack of the fluoride on the alkyl groups were a limitation. This led us to contemplate metals as reducing agents with the possibility that solvation of the metal cation formed by the solvent would provide an additional driving force. Acetonitrile proved to be an almost ideal solvent for the purpose. It is relatively easily purified,

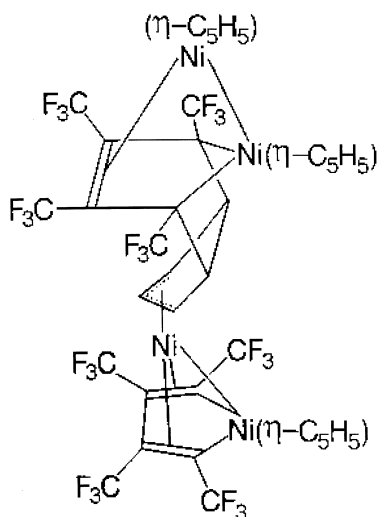
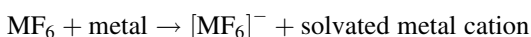


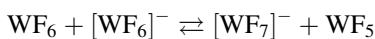
Fig. 3. Structure of the black crystalline tetramer $[\text{Ni}(\text{Cp})\text{CF}_3\text{C}_2\text{CF}_3]_4$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$). (Reproduced, with permission, from Ref. [61]).

has a convenient liquid range and a relatively high dielectric constant. Anions, even F^- [22], are poorly solvated in this solvent, but a range of d-block and post-d cations, particularly those with a d^{10} electronic configuration, are solvated moderately well.

Our initial success owed much to Ann Prescott, who came to Glasgow in 1971 (from Leeds University) as a research fellow with a background in non-aqueous solution chemistry. Her initial survey focused on the oxidation of 3d and post-d metals by MoF_6 or WF_6 in MeCN. Both hexafluorides are $1e^-$ oxidants in MeCN, but the behaviour of WF_6 is complicated by its ability to react with $[WF_6]^-$ generating the $[WF_7]^-$ anion [72].



(M = Mo, W)



Although salts of $[WF_7]^-$ were isolated with Tl^+ or Cu^{II} counter-cations, as part of this study the complex $WF_5(NCMe)$ was not satisfactorily identified until much later [73]. The actinide hexafluoride UF_6 in MeCN has similar redox and F^- ion acceptor properties, although it is slowly reduced by MeCN to give U^V [74,75].

These observations were placed on a firm thermodynamic basis by Graham Heath (University of Stirling, then Edinburgh) and David Sharp, who undertook a comprehensive examination of redox behaviour of 4d and 5d Group 1 hexafluorometallates (V) by cyclic voltammetry. Successive E^0 values for the couples $[MF_6]^{z/z-1}$, $z = 0, -1, -2$, when M = Ta, W, Re, Os and Ir or Nb, Mo and Ru, show a remarkable linear progression. Oxidizing power increases with increasing d^n configuration, the 4d member being significantly more oxidizing than its 5d counterpart. The linear relationships appear to be the result of central-metal core charge and configuration and deviations (Fig. 4) are observed at d^3/d^4 couples due to spin-pairing effects [76]. The pleasingly-simple pattern is replicated for analogous chloro-metallates in CH_2Cl_2 [77]. This work, together with cyclic voltammetry measurements of hexafluorometallates (V) having redox active cations [78], led to the order of oxidizing ability in MeCN, $UF_6 > MoF_6 > [NO]^+ >$ solvated $Cu^{2+} \geq WF_6$ and to the identification of redox and F^- ion transfer equilibria in the system Cu metal/solvated Cu^{n+} ($n = 1$ or 2)/ $WF_6/[WF_6]^-$. The quantitative difference (ca 1.1 V) between the thermodynamic oxidizing abilities of MoF_6 and WF_6 in MeCN is virtually identical with these fluorides' properties in anhydrous HF, work undertaken by Tom O'Donnell's group in Melbourne⁶, and is consistent

⁶Tom O'Donnell and his group kept the fluorine flag flying in Australia (University of Melbourne) throughout the 1960s, 1970s and 1980s. His physical-inorganic studies of solute behaviour in anhydrous HF are regarded highly. Irene Irvine, a Glasgow graduate, undertook some of the early work on WF_6 and MoF_6 in HF as part of her Ph.D. studies with Tom. He and his redoubtable wife, Pat are inveterate world travellers, so we still have frequent contacts.

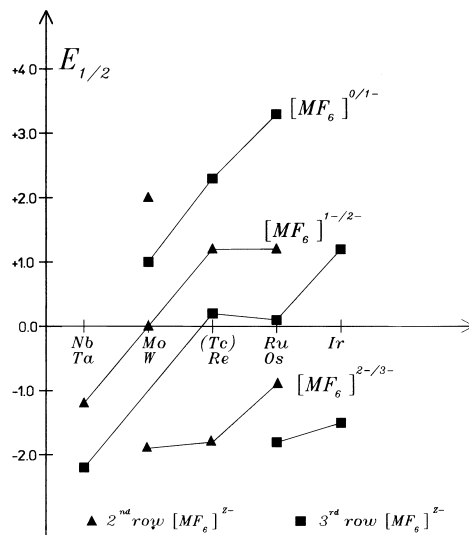


Fig. 4. $E_{1/2}/V$ versus S.C.E. data for second and third row d block $[MF_6]^{z/z-1}$ couples in MeCN. (Redrawn, with permission, from data in Ref. [76]).

with solvation effects being relatively unimportant in these redox couples.

There were two immediate consequences of the work described above: firstly studies to determine whether UF_6 , MoF_6 and WF_6 could be used to oxidize non-metallic elements in MeCN, and secondly, explorations of the coordination chemistry of selected metals using the solvated-metal-cation fluoroanion salts as starting materials. Elemental iodine is oxidised by UF_6 or MoF_6 , but not by WF_6 , in MeCN below room temperature to give the $[I(NCMe)_2]^+$ cation [79], shown to have a linear N-I-N skeleton by I K-edge EXAFS [80]. This redox behaviour is in contrast to the situation in IF_5 , where I_2 is oxidised by UF_6 or ReF_6 , but not MoF_6 , to give the I_2^+ cation [69]. Dibromine reacts with UF_6 but not with MoF_6 , in MeCN under similar conditions but evidently Br^+ is too electrophilic to exist as a simple cation solvated by MeCN and oligomerization of MeCN occurs to give a N-Br heterocyclic cation [81]. Similarly, attempts to prepare the solvated Te^{IV} cation, by oxidation of Te by UF_6 or MoF_6 , resulted in $[TeF_3(NCMe)_2]^+$ the formation of which is rationalised by F^- transfer from $[MF_6]^-$, M = Mo, U to Te^{4+} [82]. Similar behaviour is observed for other heavy p-block elements; for example the solvated Bi^{III} cation appears to have marginal kinetic stability, but fluoride ion transfer can be prevented by coordination of the macrocyclic N_4 ligand, 1,4,8,11-tetraazacyclotetradecane to Bi^{III} [83].

Our interests in coordination chemistry in MeCN derived from solvated metal cations have centred on thallium [78,84] and copper [78,85], for which two oxidation states are accessible and where oxidation reactions by Cu^{II} or Tl^{III} can be studied [86,87] and on the stepwise ligand replacement reactions of coordinated MeCN, NH_3 or py by $P(OMe)_3$ at the Fe^{II} centre [88–90]. Solvated cation/fluoroanion salts were prepared either by direct oxidation of the

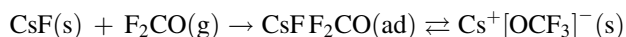
metal using MoF₆ and WF₆, or, for Cu^{II} and Fe^{II}, by acid-base reactions between the anhydrous metal fluorides and PF₅. More recently, replacement of weakly-coordinated MeCN by macrocycles at Cu^{II}, Fe^{II}, Fe^{III}, I^I and Bi^{III} centres has been studied [83,91]. As expected, replacement of the weak MeCN ligand by a macrocycle has profound effects. Stabilization of Bi^{III} by this means was referred to above [83]; a second example is that the Fe^{III} oxidation state, which is not accessible from [Fe(NCMe)₆]²⁺ in MeCN by hexafluoride oxidation [88], is formed by oxidation of [FeL(NCMe)₂]²⁺, L = [12]aneN₄ or [14]aneN₄, using the weak oxidant PF₅ [91]. Similarly, oxidation of [Agpy₄]⁺ or [Agpy₂]⁺ cations by MoF₆ or UF₆, respectively, leads to Ag^{III} species, whereas Ag^I solvated by MeCN is not oxidised [92].

6. Fluorine-18 radiotracer studies: catalysis by fluoride ion and the liability of covalently-bound fluoride ligands

Glasgow is associated with the pioneering work by Soddy and Cranston during the period 1904–1912 which led to the first isolation of the element protactinium; the term ‘isotope’ was coined by Soddy at a dinner party held in a house on University Avenue. Since then, the use of isotopes for the investigation of various chemical phenomena has been a Glasgow tradition. The only feasible fluorine isotope for use as a tracer is fluorine-18, a β⁺ emitter whose t_{1/2} is 110 min. Our use of the isotope dates from the early 1970s following conversations between the author and Geoff Webb, a Glasgow colleague whose research interests included the application of [¹⁴C] labelling for the study of heterogeneous catalysis by oxide-supported transition metals. Enthused by G.H. Cady’s work on heterogeneous catalytic fluorination of CO and F₂CO, we chose to apply the [¹⁸F] tracer method to heterogeneous catalysis by F[−] anion.

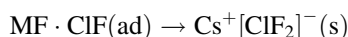
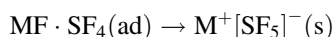
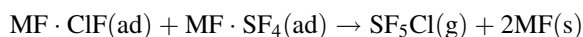
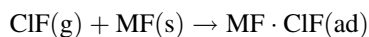
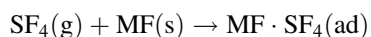
In the initial phase of the work, it was established that the extent of the interaction between solid Group 1 fluorides and [¹⁸F]-labelled SF₄, F₂CO or CF₃C(O)F followed the order Cs > Rb > K > Na, Li and, in the case of F₂CO, was enhanced by the presence of acetonitrile or diglyme [93,94]. These observations are in harmony with the behaviour of Group 1 fluorides as catalytic sources of F[−] ion, however, extension of the work to other ionic fluorides [95,96] indicated that simple correlations, for example with cation size, were not appropriate. Progress resulted by examining the effect of Group I fluoride activation on their B.E.T. areas, particularly that of CsF [97,98], and by studying Lewis base-acid interactions between activated CsF and SF₄, F₂CO and CO₂ using both [¹⁸F] and [³⁵S] or [¹⁴C] (both β[−] emitters) as appropriate [98]. Pretreatment of CsF by thermal decomposition of its 1 : 1 adducts with (CF₃)₂CO or F₂CO leads to increased B.E.T. areas, from 0.31–0.19 to 3.01–2.09 m²g^{−1}, possibly due to the development of some degree of meso- or macro-porous structure. Reactions

between activated CsF and SF₄ or F₂CO involve both weakly adsorbed and strongly bound species, and can be described as follows [98]:



Although adsorption of ¹⁴CO₂ on activated CsF was detected, no complex was isolated. Other solid F[−] anion sources that were characterised in this way are CsF or KF supported on calcined γ-alumina [99] or on fluorinated γ-alumina [100], the latter being useful when a non-hydroxylic material of relatively high B.E.T. area is required.

Using a combination of [³⁶Cl] and [³⁵S] radiotracers enabled the progress of the room-temperature chlorofluorination of SF₄ by ClF to be followed and the mechanism of the catalysis involving CsF [101] or Cs⁺ or K⁺ fluorides supported on fluorinated γ-alumina [102] to be determined. Caesium fluoride supported on fluorinated γ-alumina, loading 5.5 mmol g^{−1}, has catalytic activity which is comparable with that of unsupported activated CsF; supported KF although less active, has acceptable activity. The mechanism is identical in all cases [101,102] and can be described as follows:



in which formation of [SF₅][−] and, particularly, [ClF₂][−] result in catalyst poisoning.

The radioisotope [¹⁸F] has proved to be a useful complementary technique to ¹⁹F NMR spectroscopy to study fluorine exchange, being particularly suited to situations in solution where exchange may be slow on the NMR time scale and to the study of weak interactions occurring under heterogeneous conditions. The extent of [¹⁸F] exchange in solution between Me₃Si¹⁸F and various substituted derivatives of high-oxidation-state fluorides depends both on the identity of the central atom and on the number and nature of the substituents; for example, with W^{VI} and the MeO-substituent, exchange rates vary in the order WF₆ < WF₅(OMe) > *cis*-WF₄(OMe)₂ > WF₃(OMe)₃ > *cis*-WF₂(OMe)₄; associative mechanisms have been formulated [103]. Exchange was also observed with MoF₆, IF₅, IF₄(OMe) [103] UF₆ and β-UF₅ [104], although not with TeF₆ or TeF₅(OMe) [103]. [¹⁸F] Exchange reactions between the hexafluorides of Mo, W and U and various fluoro-anions have established that fluorine in [SbF₆][−] and to some extent in [AsF₆][−] is less labile than fluorine in [BF₄][−] or in other hexafluorometallates(V) [105]. The isotope [¹⁸F] has been used also to demonstrate that [MoF₇][−] and [WF₇][−] anions co-exist with their hexafluorides in MeCN at room tem-

perature [106]. Surface complexation of SF₄, labelled with [¹⁸F] or [³⁵S], with solid AlF₃, CrF₃ and MF₅, M = Nb, Ta or U is rationalised on the basis of [SF₃]⁺ formation [107], although isolable complexes were not formed under the conditions used (c.f. its behaviour towards CsF described above [98]).

7. Chlorofluorocarbons and their alternatives

Our interest in heterogeneous catalytic fluorination of a C–Cl bond to a C–F bond dates from a request from ICI in the early 1980s to determine whether using [¹⁸F] labelling would throw any light on the processes occurring during the HF pretreatment of chromia catalysts prior to their use for the large scale production of chlorofluoroethanes, C₂Cl_{6–n}F_n, particularly where *n* = 3, 4, or 5. We found that labelling experiments using H¹⁸F were ideal for the purpose and by [¹⁸F] exchange between HF vapour and [¹⁸F] – labelled fluorinated chromia catalysts, proposed the existence of three types of surface fluorine-containing species: weakly adsorbed, catalytically active, and inert. The differing behaviour observed over a catalyst's lifetime was rationalised on the basis of a slow replacement of Cr^{III}–O by Cr^{III}–F bonds [108]. Catalytic fluorination of C₂Cl₄ + Cl₂ (≡C₂Cl₆) by HF over fluorinated chromia at ≥623 K characteristically produces mixtures of C₂Cl_{6–n}F_n (*n* = 1–5) even when an excess of HF is present. [¹⁸F] Labelling experiments established that the radioisotope was incorporated into the products from the fluorinated catalyst [109], and [³⁶Cl]-labelling showed that a parallel phenomenon occurred, even though the chlorine-containing species was present on the catalyst to a very small extent [110]. This indicates that the reaction should be viewed as two distinct processes, fluorination of C–Cl to C–F and chlorination of C–F to C–Cl, a suggestion first made by Professor J.C. (Colin) Tatlow in 1974, rather than the more conventional dismutation processes. Further work on this system in which the [¹⁸F] or [³⁶Cl] activities in individual products were determined by radio-G.C., resulted in a refinement of the halogen-exchange proposal and a model for the dynamic behaviour of chlorofluoroethanes on fluorinated chromia [111] (Fig. 5). In this model, catalytic fluorination and catalytic chlorination are both viewed as intermolecular processes in which the catalytically-active Cl originates from C–Cl as a result of the fluorination step. There is no requirement, however, for chlorination and fluorination to be concerted, as would be the case for a dismutation. In contrast, isomerizations of CCl₂FCClF₂ to CCl₃CF₃ and CClF₂CClF₂ to CCl₂FCF₃ are intramolecular, and exchange with surface halogen-containing species is not involved.

The advent of the Montreal and subsequent protocols has resulted in increased interest in heterogeneous catalytic fluorination for the synthesis of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), notably

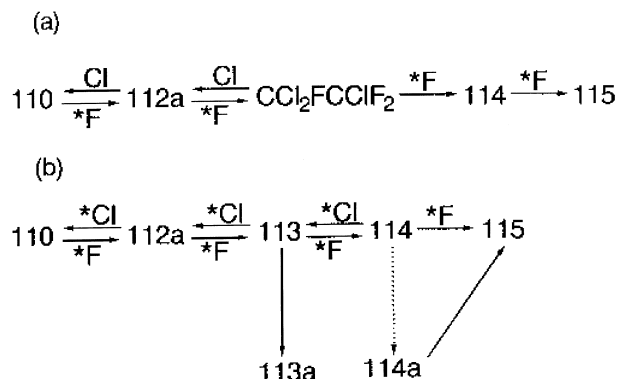


Fig. 5. Halogen exchange and isomerization reaction scheme for chlorofluoroethane behaviour on fluorinated chromia at 700 K. (a) Partial model deduced using CCl₂FCClF₂ as feedstock and catalyst labelled with [¹⁸F]. (b) Model deduced using all experimental data. F and Cl are catalytically active surface halogen species, * = radioactive. Key to compounds: 110 = C₂Cl₆, 112a = CCl₃CClF₂, 113 = CCl₂FCClF₂, 113a = CCl₃CF₃, 114 = CClF₂CClF₂, 114a = CCl₂FCF₃, 115 = CClF₂CF₃. (Reproduced, with permission, from Ref. [111]).

CF₃CH₂F, as replacements for CFC-based refrigerants. Rather unexpectedly, we discovered a room temperature heterogeneous catalytic halogen-exchange process whereby hydrochloroethanes, for example CH₃CCl₃, are converted to HCFCs [112]. The catalysts involved are based on γ-alumina, fluorinated with SF₄ to promote surface activity and to provide a ‘pool’ of labile fluorine [113] then treated with CH₃CCl₃ (which undergoes dehydrochlorination with subsequent oligomerization of the CH₂ = CCl₂ formed) to give an organic-layer supported on the fluorinated oxide surface [112]. Our model for the behaviour of these oxide-supported organic layer catalysts in reactions such as CH₃CCl₃ + HF → CH₃CCl₂F + HCl is that the organic-layer provides a quasi-liquid medium to trap the reactant, CH₃CCl₃; the latter undergoes dehydrochlorination at strongly Lewis-acidic sites on the fluorinated oxide surface, and CH₂ = CCl₂ so formed is hydrofluorinated to give CH₃CCl₂F. Labile fluoride on the catalyst is replenished by HF [114]. Catalytic fluorination at room temperature using fluorinated Fe₃O₄ and Co₃O₄ occurs in a similar manner, but where the organic substrate does not undergo dehydrochlorination readily, radical intermediates are believed to be involved [115].

8. Conclusions — current research activities

Our interest in CFC alternatives continues and is increasingly focused on catalysis involving CF₃CH₂F, both its formation via the heterogeneous catalytic fluorination of CF₃CH₂Cl, and the ways in which it might be activated catalytically to generate new chemistry. In this context, calculations to determine its Brønsted acidity have been carried out [116].

Chemical–mechanical polishing, the process whereby surface roughness of electronic, optical or electro-optic

materials is removed prior to the use of these materials in device manufacture, is usually regarded as the province of engineers; however, chemists do have a role to play in characterization of the surface etching processes that are involved. Halogen-containing compounds are important etchants and much of our work has been concerned with the role of the $[\text{HF}_2]^-$ anion, using ^{18}F to probe the surface events. Polishing of the ferroelectric LiNbO_3 is enhanced, both in terms of time and surface quality, by incorporation of $[\text{HF}_2]^-$ in the conventional silica sol polishing reagent. The reason is that LiNbOF_4 is formed as an intermediate and is readily hydrolysed under the aqueous medium polishing conditions used to give sparingly-soluble Nb_2O_5 as one product [117]. The $[\text{HF}_2]^-$ anion is also implicated in a process for the rapid polishing of silica using an $[\text{HF}_2]^-$ ceria mixture at low pH. In this process the intermediate is a K_2SiF_6 particle which is coated with a thin silica layer [118]. Silica wafers polished in this way are excellent substrates for the deposition of thin films of polycyclic hydrocarbons, which in turn may be modified chemically by adsorption of MoF_6 , WF_6 or AsF_5 [119].

Theoretical studies of small, highly endothermic, non-metal species, including fluorides, became a new Glasgow interest with the arrival of T.M. (Thomas) Klapoetke from Berlin in 1995 to occupy the Ramsay Professorship of Chemistry. Since azides are his major interest, we became quite used to the occurrence of small (controlled!) explosions from his laboratory [120]; his work includes the study of cations such as $[\text{ICNI}]^+$, as its $[\text{AsF}_6]^-$ salt [121] and intermediates such as $\text{FXe}(\text{N}_3)$ [122]. More conventional chemistry includes a modified laboratory synthesis of AuF_3 [123], a ‘Cambridge’ compound prepared using BrF_3 [3]. Collaborative work with Tom Klapoetke continues since his return to Germany in 1997 to become Head of the Institute for Inorganic Chemistry at the University of Munich.

Fluorine research at Glasgow today, although very different in character than that of the 1960s, continues to survive and thrive in the uncertain climate of funding that is prevalent in UK Universities. The work that has been reviewed here would not have been possible without the enormous contributions made by talented and enthusiastic students and research assistants. Many have gone on to pursue academic careers, either continuing with fluorine chemistry or changing to other fields. Others have pursued radically different careers; David Sharp’s former students, for example, include two ordained members of the Churches of England and Scotland. Sadly, the careers of four former colleagues, John Fuggle, Gerry Oates, Matt Baillie and Andrew Lane, were cut short by their untimely deaths. There is no telling where a ‘fascination with fluorine’ will lead.

Acknowledgements

I am very grateful to those who have helped in compiling this account of Fluorine Chemistry at Glasgow, particularly

Drs M. Mercer and A.A. Woolf who provided personal memoirs and Prof. D.W.A. Sharp, with whom I have reminisced much about the ‘early days’ and who cast a critical eye over the manuscript.

Appendix A. Recollections of early days in the Cambridge Inorganic Lab by A.A. Woolf, Faculty of Applied Science, University of the West of England, Bristol, BS16 1QY, UK

Emeléus was appointed Professor of Inorganic Chemistry in Cambridge in 1945 and commenced work there during a period of considerable austerity, albeit one of great expectations (1945–1947). The student body at that time was reinforced by a more mature and experienced set of wartime returnees who had left after the Part I Tripos (2nd year examinations) and were keen to make up for the lost time and complete their courses. Inorganic research was a very junior partner to Todd’s organic activities and was allocated only half a teaching laboratory and a few off-rooms. Emeléus started up with three students from Imperial College (A.A. Banks, A.G. Maddock and D.S. Payne), two ICI employees from Runcorn (V. Kerrigan and Davies), an experienced fluorine chemist from Birmingham University (R.N. Haszeldine), and the first Cambridge graduate (A.G. Sharpe).

Present day essentials such as IR, MS, NMR, GC, HPLC etc. were absent, weighing was by swings rather than push-button, and the most advanced instrument was a new Beckmann UV–Vis spectrometer. As far as fluorine chemistry was concerned, a high-temperature fluorine cell which occasionally lifted off its base as H_2 and F_2 mixed explosively was in use until ICI donated a tamer low-temperature cell. A few quartz vessels served for reactions since fabricated fluoroplastic tubes and valves were unavailable. (Actually the use of a quartz flask was advantageous, enabling the key compound CF_3I to be made from Cl_4 and IF_5 ; previous use of copper vessels caused Ullmann coupling to C_2F_6 .) The main innovation introduced by Emeléus was the use of vacuum systems for most of the work. The ones made for Si and B hydride chemistry employed Stock mercury float valves, and Emeléus relaxed in the summer by cutting down systems, cleaning and rejoining them all in the difficult-to-work soft glass. Other students set up their own Pyrex systems with conventional taps. Volatile compounds were purified by trap-to-trap vacuum distillation using a series of slush (cooling) baths and identified by vapour pressure measurements and molecular weight determination using gas density bulbs (Regnault’s method). Fluorine analyses were by long-winded CaF_2 gravimetry, or the less precise $\text{Th}(\text{NO}_3)_4$ titrimetry after Willard–Winter distillation, since the fluoride electrode had yet to be invented. Most of the fluorochemicals were not obtainable commercially and had to be

home-made. No doubt the laboratory would have failed today's stringent safety regulations: liquid oxygen was used as a coolant and this caused a few bangs when one was making up slush baths with organic solvents; the extensive use of mercury in manometers and valves probably resulted in an appreciable level in the lab atmosphere; and waste fluorine was not trapped too efficiently, causing a penetrating odour reminiscent of hypochlorous acid or ozone in the cell room, especially when the wind was in the wrong direction.

The build up of inorganic research student numbers continued with Cambridge graduates (me and J. Banus in 1947 followed by F.W. Bennett and F.G.A. Stone in 1948) and an overseas contingent [R.L. Martin, N.N. Greenwood (Australia), V. Gutmann (Austria), Gambroya (Spain), and G. Brandt (Finland)] of whom six were involved in fluorine chemistry. Supervision was more of a term-by-term rather than a daily event, since Emel us would suggest a starting project and leave the student to get on with it. Only if results were not forthcoming would he suggest an alternative or persuade another student to transfer a working project (this was quite feasible in the co-operative and relaxed atmosphere which prevailed in the lab). Researchers were also allowed to develop their own projects, within available resources. Looking back, it is remarkable that so much could be achieved without the sophisticated equipment and facilities available today; and of course it was much more affordable then.

Appendix B. Chemistry at Birmingham in the 1960s by Mary Mercer

Advice on how to select a research supervisor came from a very young Professor in Ottawa: "You start at the top and work your way downwards" he stated, handing me a list of British inorganic chemists in what he claimed was their order of merit. Twelve applications and eight offers later, more advice was required: "You have to choose between being happy and going to Oxford," was his second effort, followed by a thumb-nail sketch-unprintable-of what each of the potential candidates for my services would be like to work for. It was on this promising note that in 1961 I found myself in the laboratories of a certain Dr. R.D. Peacock at Birmingham University, with the proximity of the Welsh mountains the main week-end attraction.

Ray Peacock had gone into fluorine chemistry in its early days, when passing fluorine over a new element was all that was needed to get a Ph.D.: anything that came out the other end was a new compound. By the time I arrived on the scene it was getting slightly harder. George Hargreaves was before my time, but copies of his thesis dealing mainly with complex fluorides — a truly massive tome—remained behind in every lab, supposedly to act as a guide to the next

generation on the quantity of work we, too, were expected to produce. Each new student was given a compound, with instructions to determine its chemical properties. John Holloway had RuF_5 ; Dave Hugill had TcF_6 , and was locked up in a little room alone with it, with instructions not to let it out; John Holmes was working on tin compounds; Vijayan Nayar had TiCl_4 to start with; and I was presented with WF_6 , a substance chiefly remarkable for not being as reactive as MoF_6 . Tony Edwards, then a research fellow from Imperial College, spent his days painstakingly growing single crystals by subliming volatile solids such as MoF_5 , VF_5 , NbF_5 , TaF_5 , WOF_4 , MoOF_4 and ReOF_4 . These were coaxed up very fragile glass tubes in the faint hope that one of them would be a perfect crystal and land obligingly at least a millimetre away from anything else.

In the spring of 1964, with my thesis soon due in, my grant was running out and my landlady was pressing for the rent, (Bernie Cohen, an American research fellow, lent me £50, which kept me going for 3 months), and I needed to do something novel with WF_6 . One day as I sat cross-legged on the bench watching my neighbour Vijayan Nayar doing chemistry Indian style with TiCl_4 , I wondered aloud what would happen if our two compounds were mixed together, 'Absolutely nothing', opined by labmates unanimously, 'They're both d^0 configurations so they can't possibly react.' My despised reaction went with violent enthusiasm, and Bernie came on the scene to help design the apparatus for measuring the physical properties of the product WF_5Cl , the first chlorofluoride of tungsten.

With Ray's departure for Leicester the whole group broke up. Tony stayed at Birmingham. John followed Ray to Leicester, after some years in Aberdeen. I ended up in Glasgow, working for David Sharp after satisfying my yearning to see the world via Australia. Chemistry moved into the age of the computer, and safety regulations stifled the enterprise of the more exuberant fluorine chemists.

References

- [1] A.G. Sharpe, H.J. Emel us, *J. Chem. Soc.* (1948) 2135.
- [2] A.A. Woolf, H.J. Emel us, *J. Chem. Soc.* (1949) 2865.
- [3] A.G. Sharpe, *J. Chem. Soc.* (1949) 2901.
- [4] A.G. Sharpe, *J. Chem. Soc.* 2907 (1950) 3444.
- [5] A.G. Sharpe, A.A. Woolf, *J. Chem. Soc.* (1951) 798.
- [6] A.G. Sharpe, *J. Chem. Soc.* (1952) 4538.
- [7] A.G. Sharpe, *J. Chem. Soc.* (1953) 197.
- [8] R.D.W. Kemmitt, D.W.A. Sharp, *J. Chem. Soc.* (1961) 2496.
- [9] R.S. Nyholm, A.G. Sharpe, *J. Chem. Soc.* (1952) 3579.
- [10] B. Cox, A.G. Sharpe, *J. Chem. Soc.* (1953), 1783.
- [11] B. Cox, *J. Chem. Soc.* (1954) 3251.
- [12] B. Cox, *J. Chem. Soc.* (1956) 876.
- [13] R.D.W. Kemmitt, D.R. Russell, D.W.A. Sharp, *J. Chem. Soc.* (1963) 4408.
- [14] D.H. Brown, K.R. Dixon, R.D.W. Kemmitt, D.W.A. Sharp, *J. Chem. Soc.* (1965) 1559.
- [15] D.W.A. Sharp, N. Sheppard, *J. Chem. Soc.* (1957) 674.
- [16] R.D. Peacock, D.W.A. Sharp, *J. Chem. Soc.* (1959) 2762

- [17] D.H. Brown, K.R. Dixon, C.M. Livingston, R.H. Nuttall, D.W.A. Sharp, *J. Chem. Soc. (A)*. (1967) 100.
- [18] A.P. Lane, D.W.A. Sharp, *J. Chem. Soc. (A)*. (1969) 2942
- [19] A.P. Lane, D.W.A. Sharp, J.M. Barraclough, D.H. Brown, D.A. Patterson, *J. Chem. Soc. (A)*. (1971) 94.
- [20] A.G. Sharpe, *Adv. Fluorine Chem.* 1 (1960) 29.
- [21] A.G. Sharpe, in: *Inorganic Chemistry*, 3rd edn., Longman, 1992, pp. 231, 409.
- [22] A.G. Sharpe, *J. Chem. Educ.* 67 (1990) 309.
- [23] D.S. Payne, *Quart. Rev.* 15 (1961) 173.
- [24] T. Kennedy, D.S. Payne, *J. Chem. Soc.* (1960) 4126.
- [25] D.H. Brown, G.W. Fraser, D.W.A. Sharp, *J. Chem. Soc. (A)* (1966) 171.
- [26] D.H. Brown, K.D. Crosbie, G.W. Fraser, D.W.A. Sharp, *J. Chem. Soc. (A)* (1969) 551.
- [27] J.S. Harman, D.W.A. Sharp, *J. Chem. Soc. (A)* (1970) 1138.
- [28] D.H. Brown, K.D. Crosbie, G.W. Fraser, D.W.A. Sharp, *J. Chem. Soc. (A)* (1969) 872.
- [29] D.H. Brown, K.D. Crosbie, J.I. Darragh, D.S. Ross, D.W.A. Sharp, *J. Chem. Soc. (A)* (1970) 914.
- [30] C.B. Colburn, W.E. Hill, D.W.A. Sharp, *J. Chem. Soc. (A)* (1970) 2221.
- [31] J.S. Harman, M.E. McCartney, D.W.A. Sharp, *J. Chem. Soc. (A)* (1971) 1547.
- [32] M.E. Harman, R. Keat, D.W.A. Sharp, *J. Inorg. Nucl. Chem. Supplement*, 1976, 49.
- [33] A.M. Noble, J.M. Winfield, *J. Chem. Soc. A* 501 (1970) 2574.
- [34] W. McFarlane, A.M. Noble, J.M. Winfield, *J. Chem. Soc. (A)* (1971) 948.
- [35] A. Majid, R.R. McLean, D.W.A. Sharp, J.M. Winfield, *Z. Anorg. Allg. Chem.* 385 (1971) 85.
- [36] A. Majid, D.W.A. Sharp, J.M. Winfield, I. Hanley, *J. Chem. Soc. Dalton Trans.* (1973) 1876.
- [37] J.C. Fuggle, D.W.A. Sharp, J.M. Winfield, *J. Chem. Soc. Dalton Trans.* (1972) 1766.
- [38] G.A. Kolta, D.W.A. Sharp, J.M. Winfield, *J. Fluorine Chem.* 14 (1979) 153.
- [39] O.R. Chambers, M.E. Harman, D.S. Rycroft, D.W.A. Sharp, J.M. Winfield, *J. Chem. Res. (S)* (1977) 150
- [40] O.R. Chambers, M.E. Harman, D.S. Rycroft, D.W.A. Sharp, J.M. Winfield, *J. Chem. Res. (M)* (1977) 1849.
- [41] J.I. Darragh, D.W.A. Sharp, *Angew. Chem.* 82 (1970) 45.
- [42] D.S. Ross, D.W.A. Sharp, *J. Chem. Soc. Dalton Trans.* (1972) 34.
- [43] J.I. Darragh, S.F. Hossain, D.W.A. Sharp, *J. Chem. Soc. Dalton Trans.* (1975) 218.
- [44] J.I. Darragh, G. Haran, D.W.A. Sharp, *J. Chem. Soc. Dalton Trans.* (1973) 2289.
- [45] G. Oates, J.M. Winfield, *J. Chem. Soc. Dalton Trans.* (1974) 119.
- [46] J.A. Berry, G. Oates, J.M. Winfield, *J. Chem. Soc. Dalton Trans.* (1974) 509.
- [47] G. Oates, J.M. Winfield, O.R. Chambers, *J. Chem. Soc. Dalton Trans.* (1974) 1380.
- [48] G.W. Fraser, J.B. Millar, *J. Chem. Soc. Dalton Trans.* (1974) 2029.
- [49] G.W. Fraser, G.D. Meikle, *J. Chem. Soc. Perkin Trans. 2* (1975) 312.
- [50] G.W. Fraser, G.D. Meikle, *J. Chem. Soc. Dalton Trans.* (1977) 1985.
- [51] G.W. Fraser, G.D. Meikle, *J. Chem. Soc. Perkin Trans. 1* (1979) 2005.
- [52] G.W. Fraser, G.D. Meikle, *J. Chem. Soc. Chem. Commun.* (1974) 624.
- [53] G.W. Fraser, J.B. Millar, *J. Chem. Soc. Dalton Trans.* (1972) 1113
- [54] J.L. Davidson, D.W.A. Sharp, *J. Chem. Soc. Dalton Trans.* (1972) 107.
- [55] J.L. Davidson, D.W.A. Sharp, *J. Chem. Soc. Dalton Trans.* (1973) 1957
- [56] J.L. Davidson, D.W.A. Sharp, *J. Chem. Soc. Dalton Trans.* (1975) 813.
- [57] G. Haran, D.W.A. Sharp, *J. Chem. Soc. Perkin Trans. 1* (1972) 34.
- [58] J.L. Boston, D.W.A. Sharp, G. Wilkinson, *J. Chem. Soc.* (1962) 3488.
- [59] J.L. Davidson, D.W.A. Sharp, *J. Chem. Soc. Dalton Trans.* 2283 (1975) 2531.
- [60] P.S. Braterman, J.L. Davidson, D.W.A. Sharp, *J. Chem. Soc. Dalton Trans.* (1976) 241.
- [61] J.L. Davidson, D.W.A. Sharp, *J. Chem. Soc. Dalton Trans.* (1976) 1123.
- [62] D.W.A. Sharp, A.G. Sharpe, *J. Chem. Soc.* (1956) 1855–1858.
- [63] M.J. Baillie, D.H. Brown, K.C. Moss, D.W.A. Sharp, *J. Chem. Soc. (A)* (1968) 104.
- [64] H.J. Clase, A.M. Noble, J.M. Winfield, *Spectrochim. Acta, Part A*, 25 (1969) 293.
- [65] R.R. McLean, D.W.A. Sharp, J.M. Winfield, *J. Chem. Soc. Dalton Trans.* (1972) 676.
- [66] M. Mercer, T.J. Ouellette, C.T. Ratcliffe, D.W.A. Sharp, *J. Chem. Soc. (A)* (1969) 2532.
- [67] J.C. Fuggle, D.W.A. Sharp, J.M. Winfield, *J. Fluorine Chem.* 1 (1971/72) 427.
- [68] J.C. Fuggle, D.A. Tong, D.W.A. Sharp, J.M. Winfield, J.H. Holloway, *J. Chem. Soc. Dalton Trans.* (1974) 205.
- [69] J.A. Berry, A. Prescott, D.W.A. Sharp, J.M. Winfield, *J. Fluorine Chem.* 10 (1977) 247.
- [70] J.A. Berry, D.W.A. Sharp, J.M. Winfield, *J. Chem. Res. (S)* (1978) 377
- [71] J.A. Berry, D.W.A. Sharp, J.M. Winfield, *J. Chem. Res. (M)* (1978) 4664.
- [72] A. Prescott, D.W.A. Sharp, J.M. Winfield, *J. Chem. Soc. Dalton Trans.* 934 (1975) 936.
- [73] N. Bao, J.M. Winfield, *J. Fluorine Chem.* 50 (1990) 339.
- [74] J.A. Berry, R.T. Poole, A. Prescott, D.W.A. Sharp, J.M. Winfield, *J. Chem. Soc. Dalton Trans.* (1976) 272.
- [75] D.K. Sanyal, D.W.A. Sharp, J.M. Winfield, *J. Fluorine Chem.* 19 (1981/82) 55.
- [76] S. Brownstein, G.A. Heath, A. Sengupta, D.W.A. Sharp, *J. Chem. Soc. Chem. Commun.* (1983) 669.
- [77] G.A. Heath, K.A. Moock, D.W.A. Sharp, L.J. Yellowlees, *J. Chem. Soc. Chem. Commun.* (1985) 1503.
- [78] G.M. Anderson, J. Iqbal, D.W.A. Sharp, J.M. Winfield, J.H. Cameron, A.G. McLeod, *J. Fluorine Chem.* 24 (1984) 303.
- [79] G.M. Anderson, J.M. Winfield, *J. Chem. Soc. Dalton Trans.* (1986) 337.
- [80] C.D. Garner, L. McGhee, A. Steel, J.M. Winfield, *J. Fluorine Chem.* 69 (1994) 73.
- [81] L. McGhee, D.S. Rycroft, J.M. Winfield, *J. Fluorine Chem.* 36 (1987) 351.
- [82] L. McGhee, J.M. Winfield, *J. Fluorine Chem.* 57 (1992) 147.
- [83] S.I. Ajiboye, J. Iqbal, R.D. Peacock, N. Prouff, G.J. Taylor, J.M. Winfield, X. Liu, *J. Fluorine Chem.* 91 (1998) 213.
- [84] R.M. Siddique, J.M. Winfield, *J. Fluorine Chem.* 40 (1988) 71.
- [85] A.C. Baxter, J.H. Cameron, A. McAuley, F.M. McLaren, J.M. Winfield, *J. Fluorine Chem.* 10 (1977) 289.
- [86] G.M. Anderson, J.H. Cameron, A.G. Lappin, J.M. Winfield, A. McAuley, *Polyhedron* 1 (1982) 467.
- [87] R.M. Siddique, J.M. Winfield, *Can. J. Chem.* 67 (1989) 1780.
- [88] C.J. Barbour, J.H. Cameron, J.M. Winfield, *J. Chem. Soc. Dalton Trans.* (1980) 2001.
- [89] J.H. Cameron, A.G. Lappin, J.M. Winfield, A. McAuley, *J. Chem. Soc. Dalton Trans.* (1981) 2172.
- [90] L. McGhee, R.M. Siddique, J.M. Winfield, *J. Chem. Soc. Dalton Trans.* (1988) 1309.

- [91] S.H. Wang, S.I. Ajiboye, G. Haining, L. McGhee, R.D. Peacock, G. Peattie, R.M. Siddique, J.M. Winfield, *J. Chem. Soc. Dalton Trans.* (1995) 3837.
- [92] J. Iqbal, D.W.A. Sharp, J.M. Winfield, *J. Chem. Soc. Dalton Trans.* (1989) 461.
- [93] C.J.W. Fraser, D.W.A. Sharp, G. Webb, J.M. Winfield, *J. Chem. Soc. Dalton Trans.* (1972) 2226
- [94] C.J.W. Fraser, D.W.A. Sharp, G. Webb, J.M. Winfield, *J. Chem. Soc., Dalton Trans.* (1974) 112.
- [95] C.J.W. Fraser, D.W.A. Sharp, R.A. Sule, G. Webb, J.M. Winfield, *J. Chem. Res. (S)*, (1978) 2
- [96] C.J.W. Fraser, D.W.A. Sharp, R.A. Sule, G. Webb, J.M. Winfield, *J. Chem. Res. (M)* (1978) 311
- [97] C.J.W.C.J.W.G.A. Kolta, D.W.A.D.W.A.G. Webb, G.R.A.J.M. Winfield, *J. Fluorine Chem.* 14 (1979) 331.
- [98] K.W. Dixon, J.M. Winfield, *J. Chem. Soc. Dalton Trans.* (1989) 937.
- [99] T. Baird, A. Bendada, G. Webb, J.M. Winfield, *J. Mater Chem.* 1 (1991) 1071.
- [100] T. Baird, A. Bendada, G. Webb, J.M. Winfield, *J. Fluorine Chem.* 66 (1994) 117.
- [101] G.A. Kolta, G. Webb, J.M. Winfield, *Appl. Catal.* 2 (1982) 257.
- [102] T. Baird, A. Bendada, M. Selougha, G. Webb, J.M. Winfield, *J. Fluorine Chem.* 69 (1994) 109.
- [103] R.T. Poole, J.M. Winfield, *J. Chem. Soc. Dalton Trans.* (1976) 1557.
- [104] D.K. Sanyal, J.M. Winfield, *J. Fluorine Chem.* 24 (1984) 75.
- [105] M.F. Ghorab, J.M. Winfield, *J. Fluorine Chem.* 49 (1990) 367.
- [106] M.F. Ghorab, J.M. Winfield, *J. Fluorine Chem.* 62 (1993) 101.
- [107] K.W. Dixon, M.F. Ghorab, J.M. Winfield, *J. Fluorine Chem.* 37 (1987) 357.
- [108] J. Kijowski, G. Webb, J.M. Winfield, *Appl. Catal.* 27 (1986) 181.
- [109] J. Kijowski, G. Webb, J.M. Winfield, *J. Fluorine Chem.* 27 (1985) 213.
- [110] L. Rowley, G. Webb, J.M. Winfield, A. McCulloch, *Appl. Catal.* 52 (1989) 69.
- [111] L. Rowley, J. Thomson, G. Webb, J.M. Winfield, A. McCulloch, *Appl. Catal. A* 79 (1991) 89.
- [112] J. Thomson, G. Webb, J.M. Winfield, D. Bonniface, C. Shortman, N. Winterton, *Appl. Catal. A* 97 (1993) 67.
- [113] A. Bendada, G. Webb, J.M. Winfield, *Eur. J. Solid State Inorg. Chem.* 33 (1996) 907.
- [114] A. Bendada, D.W. Bonniface, F. McMonagle, R. Marshall, C. Shortman, R.R. Spence, J. Thomson, G. Webb, J.M. Winfield, N. Winterton, *Chem. Commun.* (1996) 1947.
- [115] J. Thomson, *J. Chem. Soc. Faraday Trans.* 90 (1994) 3585.
- [116] T.M. Klapoetke, J.M. Winfield, *J. Fluorine Chem.* 88 (1998) 19.
- [117] M. Beveridge, L. McGhee, S.G. McMeekin, M.I. Robertson, A. Ross, J.M. Winfield, *J. Mater Chem.* 4 (1994) 119.
- [118] D.S. Boyle, J.M. Winfield, *J. Mater. Chem.* 6 (1996) 227.
- [119] D.S. Boyle, J.M. Winfield, *J. Mater. Chem.* 7 (1997) 2039.
- [120] H. Holfter, T.M. Klapoetke, A. Schulz, *Propellants, Explosives, Pyrotechnics* 22 (1997) 51.
- [121] T.M. Klapoetke, *J. Chem. Soc. Dalton Trans.* (1997) 553.
- [122] A. Schulz, T.M. Klapoetke, *Inorg. Chem.* 36 (1997) 1929.
- [123] I.C. Tornieporth-Oetting, T.M. Klapoetke, *Chem. Ber.* 128 (1995) 957.



David Sharp has recently retired from directing the Office of International Programmes at the University of Glasgow, a post which he has held for the past 22 years. Prior to that he was the first occupant of the Ramsay Chair of Chemistry, and at various periods was Head of Department and Dean of Science. He maintains his interest in fluorine chemistry as one of the Editors of *Journal of Fluorine Chemistry* and is a regular attendee at fluorine chemistry symposia.



John Winfield holds a Personal Professorship in Inorganic Chemistry at the University of Glasgow and was currently Head of Department. His BSc and PhD degrees were awarded from the Universities of London (Imperial College) and Glasgow (Royal College of Science and Technology), respectively, in 1961 and 1964. He was appointed a lecturer at the University of Glasgow in 1965 following postdoctoral work with R.J. (Ron) Gillespie, McMaster University, Hamilton, Ontario, and has progressed through the ranks as Senior Lecturer in 1974, Reader 1985 and Professor in 1995.